

10/563539

IAP6 Rec'd PCT/PTO 20 DEC 2005

TRANSLATION OF THE ANNEX TO THE IPER

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25. The process of any one of claims 22 to 24, characterized in that reaction stages a₁) and a₂) are carried out at a temperature of from 40 to 120°C.

5 26. The process of claim 25, characterized in that the process is performed at a temperature of 50 to 110°C.

10 27. The process of any one of claims 22 to 26, characterized in that reaction stages a₃) and b) are carried out at a temperature of from 10 to 60°C.

28. The process of claim 27, characterized in that the process is carried out at a temperature of 20 to 50°C.

15 29. The process of any one of claims 22 to 28, characterized in that reaction stages c₁) and c₂) are carried out at a temperature of from -20 to 50°C.

20 30. The process of claim 29, characterized in that the process is performed at a temperature of 0 to 30°C.

25 31. The use of the fluorine-modified polyurethane resins of claims 1 to 22 in the construction or industrial sector for the permanent oil- and water-repellent surface treatment or modification of mineral and nonmineral substrates.

30 32. The use of the fluorine-modified polyurethane resins of claim 31, characterized in that the mineral and nonmineral substrates are inorganic surfaces.

35 33. The use of the fluorine-modified polyurethane resins of claim 32, characterized in that the inorganic surfaces are, for example, porous, absorbent, rough and polished construction materials and building materials of all kinds (such as concrete, gypsum, silica and silicates, artificial stone, and natural stone (such as granite, marble, sandstone, slate, and serpentine),

clay, cement, brick) and also enamels, fillers and pigments, glass, ceramic, metals and metal alloys.

34. The use of the fluorine-modified polyurethane resins of claim 31, characterized in that the mineral and nonmineral substrates are organic surfaces.

35. The use of the fluorine-modified polyurethane resins of claim 32, characterized in that the organic surfaces are, for example, wood and woodbase materials, wood veneer, glass fiber-reinforced plastics (GRP), plastics, leather, natural fibers, polar organic polymers of all kinds, or composite materials.

15 36. The use of the fluorine-modified polyurethane resins of claims 1 to 22 for the permanent oil- and water-repellent surface treatment and/or modification in the construction sector.

20 37. The use of the fluorine-modified polyurethane resins of claim 36 as

- antigraffiti/antisoiling coatings
- easy to clean coatings
- coatings of all kinds
- 25 • seals
- prefabricated concrete components
- concrete moldings
- tiles and joints
- adhesives and sealants
- 30 • soundproofing walls
- corrosion control
- renders and decorative plasters
- external insulation and finishing systems (EIFS) and external insulation systems (EIS)

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38. The use of the fluorine-modified polyurethane resins of claim 36 and 37, wherein coatings of all kinds comprise

- balcony coatings,
- roof(tile) coatings,
- baking varnishes,
- paints and varnishes,
- 5 • masonry paints,
- floor coatings,
- light-, medium- and heavy-duty industrial floors,
- carpark surfacings,
- sports floors.

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39. The use of the fluorine-modified polyurethane resins of claims 1 to 20 in the sector of

- automobile industry
- coil coatings
- 15 • baking varnishes
- glass facades and glass surfaces
- ceramics, including sanitary ceramics
- leather dressing
- surface-modified fillers and pigments
- 20 • paper coating
- rotors of wind turbines
- marine paints.

25 40. The use of the fluorine-modified polyurethane resins of claims 1 to 20 in the construction or industrial sector for the integral water/oil repellency treatment of concrete.

30 41. The concrete of claim 40, characterized in that it comprises concrete for prefabricated concrete components, concrete moldings, cast-in-place concrete, shotcrete, and ready-mix concrete.

Claims

1. A fluorine-modified one- or two-component polyurethane resin, obtainable by

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a) preparing a fluorine-modified polyurethane prepolymer having free isocyanate groups or free amino and/or hydroxyl groups, or a fluorine-modified polyol mixture having free hydroxyl groups (binder), where

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a₁) a fluorine-modified macromonomer (A1) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 2000 daltons, a higher molecular mass polyol component (A2) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 6000 daltons, and, if desired, a low molecular mass polyol component (A3)(i) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons

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either

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is reacted with a polyisocyanate component (B)(i), consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst,

25

or

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if desired, is blended in the presence of a solvent component (L)(i) and in the presence if desired of a catalyst,

a₂) the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₁) is reacted if desired with an unmodified or fluorine-modified functionalizing component (C)(i) having one or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and/or one or more isocyanate groups that are reactive toward hydroxyl groups and having a molecular mass of 50 to 2500 daltons, selected from the groups of the (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols and/or reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula (RSiO_{1.5})_n with n = 4, 6, 8, 10, 12 and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms and a molar mass of 250 to 25 000 daltons,

a₃) the fluorine-modified polyurethane prepolymer or polyol mixture from stages a₁) or a₂) is admixed with a formulating component (F)(i),

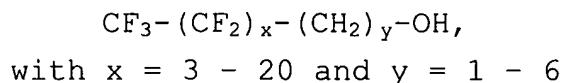
and finally

b) by preparing a fluorine-modified polyurethane resin having a polymer-bonded fluorine content of 1% to 4% by weight in the system as a whole by reacting the fluorine-modified polyurethane prepolymer from stage a₃) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a₃) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), with a formulating component (F)(ii) in the presence if desired of a solvent component (L)(iii) and also of a catalyst, using

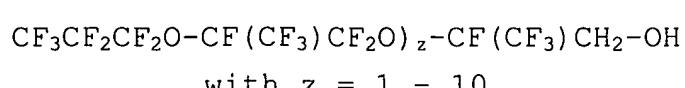
as crosslinker component (D) in the case of the polyol mixture from stage a₃) a polyisocyanate component (B)(iii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons and/or a low molecular mass polyamine component (E) having two or more (cyclo)aliphatic or aromatic amino groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons.

2. The fluorine-modified polyurethane resin of claim 1, characterized in that the fluorine-modified macro-monomer (A1) has been prepared by

c₁) reacting a fluoro alcohol component (A4) consisting of a perfluoroalkyl alcohol having terminal methylene groups (hydrocarbon spacers), of the general formula



or of a hexafluoropropene oxide (HFPO) oligomer alcohol of the general formula



or else mixtures of these having a hydroxyl group that is reactive toward isocyanate groups and

having a molecular mass of 250 to 5000 daltons, with a polyisocyanate component (B)(ii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, in the presence if desired of a solvent component (L)(ii) and in the presence if desired of a catalyst,

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c₂) if desired, reacting the preadduct from stage c₁) completely with a functionalizing component (C)(ii) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons, selected from the group of (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols.

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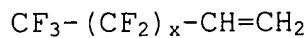
3. The fluorine-modified polyurethane resin of claim 1 or 2, characterized in that as fluorine-modified macromonomer (A1) use is made of reaction products and/or macromonomers, with a monomodal molar mass distribution, of monofunctional perfluoroalkyl alcohols, isophorone diisocyanate or toluene diisocyanate, and diethanolamine.

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4. The fluorine-modified polyurethane resin of claim 1, characterized in that as fluorine-modified macromonomer (A1) use is made of optionally solvent-containing reaction products of

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i) perfluoroalkylalkenes and diethanolamine, preferably perfluoroalkylalkenes having terminal methylene groups (hydrocarbon spacers), of the general formula



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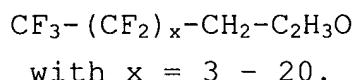
with x = 3 - 20

and/or

5 ii) alkyl (per)fluoro(meth)acrylates and/or
(per)fluoroalkyl (meth)acrylates and/or
(per)fluoroalkyl (per)fluoro(meth)acrylates and
diethanolamine

10 and/or

iii) (per)fluoroalkylalkylene oxides and N-methyl-
ethanolamine or diethanolamine with preferred
(per)fluoroalkylalkylene oxides of the general
15 formula



20 5. The fluorine-modified polyurethane resin of any
one of claims 1 to 4, characterized in that use is made
as higher molecular mass polyol component (A2) of
(hydrophobically modified) polyalkylene glycols,
aliphatic or aromatic polyesters, polycaprolactones,
25 polycarbonates, hydroxy-functional macromonomers and
telecheles such as α,ω -polymethacrylatediols, α,ω -
dihydroxyalkylpolydimethylsiloxanes, hydroxy-functional
epoxy resins, hydroxy-functional ketone resins,
hydroxy-functional polysulfides, hydroxy-functional
30 triglycerides, oxidatively drying alkyd resins based on
bisepoxides and unsaturated fatty acids, or mixtures
thereof.

6. The fluorine-modified polyurethane resin of any
35 one of claims 1 to 4, characterized in that use is made
as component (A2) of linear and/or difunctional
(hydrophobically modified) polyether- and/or polyester-
and/or polycaprolactone- and/or polycarbonate-polyols

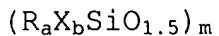
and/or α,ω -polymethacrylatediols having a molecular mass of 500 to 3000 daltons.

7. The fluorine-modified polyurethane resin of any one of claims 1 to 6, characterized in that use is made as component (A3) (i) and (A3) (ii) of 1,4-butanediol and/or 2-methyl-1,3-propanediol and/or 2,2-dimethyl-1,3-propanediol.

10 8. The fluorine-modified polyurethane resin of any one of claims 1 to 7, characterized in that use is made as components (B) (i) and/or (B) (ii) and/or (B) (iii) of difunctional polyisocyanate derivatives and/or reaction products of at least trifunctional aliphatic or aromatic polyisocyanates and optionally fluorine-modified amino-functional polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_n$ with n = 4, 6, 8, 10, 12 and R = any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms.

9. The fluorine-modified polyurethane resin of any one of claims 1 to 8, characterized in that component (C) (i) comprises reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula $(RSiO_{1.5})_8$ with R = aminopropyl and/or isocyanatopropyl and optionally $CH_2CH_2CF_2CF_2CF_2CF_2CF_3$ and/or H and/or C_1-C_{25} -alkyl and/or C_3-C_{25} -cycloalkyl and/or C_6-C_{30} -aryl and/or $(CH_2)_3(OCH_2CH_2)_nOMe$ and/or epoxypropyl and/or dimethoxysilyloxy and/or methacryloyloxypropyl and/or triethoxysilylpropyl.

35 10. The fluorine-modified polyurethane resin of any one of claims 1 to 9, characterized in that use is made as component (C) (i) of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula



with a = 0 or 1

b = 0 or 1

5 a+b = 1

m = 4, 6, 8, 10, 12,

and

R = hydrogen atom, alkyl, cycloalkyl,
10 alkenyl, cycloalkenyl, alkynyl or
cycloalkynyl group or polymer unit,
which in each case is substituted or
unsubstituted, or further functionalized
polyhedral oligomeric silicon-oxygen
cluster units, which are attached via a
15 polymer unit or a bridging unit,

X = oxy, hydroxy, alkoxy, carboxy, silyl,
alkylsilyl, alkoxyisilyl, siloxy, alkyl-
siloxyl, alkoxyisiloxyl, silylalkyl,
alkoxyisilylalkyl, alkylsilylalkyl,
20 halogen, epoxy, ester, fluoroalkyl,
isocyanate, blocked isocyanate,
acrylate, methacrylate, nitrile, amino,
phosphine or polyether group or
substituents of type R that contain at
25 least one such group of type X,

the substituents of type R and the substituents of type X each being identical or different.

11. The fluorine-modified polyurethane resin of any
30 one of claims 1 to 10, characterized in that
(cyclo)aliphatic and/or aromatic polyamines and/or
amino alcohols are used as low molecular mass polyamine
component (E).

35 12. The fluorine-modified polyurethane resin of any
one of claims 1 to 11, characterized in that latent
curing agents based on aldimines and/or ketimines

and/or enamines are used as low molecular mass polyamine component (E).

13. The fluorine-modified polyurethane resin of any
5 one of claims 1 to 12, characterized in that as
formulating component (F)(i) and (F)(ii) use is made of
defoamers, devolatilizers, lubricity and flow-control
additives, dispersing additives, substrate wetting
additives, water repellents, rheology additives,
10 coalescence assistants, matting agents, adhesion
promoters, antifreeze agents, antioxidants, UV
stabilizers, bactericides, fungicides, further
polymers, and also fillers, pigments, nanoparticles or
a suitable combination thereof.

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14. The fluorine-modified polyurethane resin of any
one of claims 1 to 13, characterized in that the NCO/OH
equivalent ratio of components (A1), (A2), (A3)(i), and
(B)(i) in stage a) is set at a level of 0.5 to 10.0,
20 preferably 1.5 to 6.0.

15. The fluorine-modified polyurethane resin of any
one of claims 1 to 14, characterized in that the NCO/OH
equivalent ratio of components (A4) and (B)(ii) in
25 stage c₁) is set at 1.9 to 2.1 and the NCO/OH+NH
equivalent ratio of the components in the preadduct
from stage c₁) and (C)(ii) in stage c₂) is set at 0.95
to 1.05.

30 16. The fluorine-modified polyurethane resin of any
one of claims 1 to 15, characterized in that the NCO/OH
equivalent ratio of binder and curing agent in stage b)
is set at a level of 1.0 to 2.0, preferably 1.0 to 1.5.

35 17. The fluorine-modified polyurethane resin of any
one of claims 1 to 16, characterized in that reaction
stages a), b), and c) are carried out in the presence
of 0.01% to 1% by weight, based on components (A) and

(B), of a catalyst which is customary for polyaddition reactions with polyisocyanates.

18. The fluorine-modified polyurethane resin of any
5 one of claims 1 to 17, characterized in that in stage
a) the solids content of fluorine-modified polyurethane prepolymer or polyol mixture, consisting of components (A1), (A2), (A3)(i), (B)(i), and (C)(i), is set at 25% to 100% by weight based on the total amount of the
10 binder, consisting of components (A1), (A2), (A3)(i), (B)(i), optionally (C)(i), (F)(i), optionally (L)(i) and optionally (L)(iii).

19. The fluorine-modified polyurethane resin of claim
15 18, characterized in that in stage a) the solids content of fluorine-modified polymethane prepolymer or polyol mixture is set at 50% to 75% by weight, based on the total amount of the binder.

20. The fluorine-modified polyurethane resin of any
one of claims 1 to 19, characterized in that in stage
b) the solids content of crosslinker component, consisting of components (B)(iii) and (B)(iii) or (A3)(ii) and/or (E), respectively, is set at 25% to
25 100% by weight, based on the total amount of curing agent (D), consisting of components (B)(iii) or (A3)(ii) and/or (E), (F)(ii) and, if desired, (L)(iii).

21. The fluorine-modified polyurethane resin of claim
30 20, characterized in that in stage b) the solids content of crosslinker component is set at 50% to 75% by weight, based on the total amount of the curing agent (D).

35 22. The fluorine-modified polyurethane resin of any one of claims 1 to 21, characterized in that the polyurethane polymer, consisting of components (A),

(B), (C), and (E), has an average molecular mass (number average) of 10 000 to 100 000 daltons.

23. A process for preparing the fluorine-modified
5 polyurethane resin of claims 1 to 22, characterized in
that

a) a fluorine-modified polyurethane prepolymer or
polyol mixture (binder) is prepared by

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a₁) reacting components (A1), (A2), and (A3)(i) either
with component (B)(i) in the presence if desired
of a solvent component (L)(i) and in the presence
if desired of a catalyst, some or all of the
15 hydroxyl groups of components (A1), (A2), and
(A3)(i) being reacted with the isocyanate groups
of component (B)(i), or blending said components
in the presence if desired of a solvent component
(L)(i) and in the presence if desired of a
20 catalyst,

20

a₂) if desired, reacting the fluorine-modified
polyurethane prepolymer or the polyol mixture from
stage a₁) with an optionally fluorine-modified
25 functionalizing component (C)(i),

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a₃) admixing the fluorine-modified polyurethane
polymer or polyol mixture from stages a₁) or a₂)
with a formulating component (F)(i), the
30 formulating constituents being added individually
or together before, during or after the reaction
or blending of the individual components, and

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b) a fluorine-modified polyurethane resin is prepared
by reacting the fluorine-modified polyurethane
prepolymer from stage a₃) in the case of a one-
component application with atmospheric moisture,
or reacting the fluorine-modified polyurethane

5 prepolymer or polyol mixture from stage a₃)
application with a crosslinker component (D)
(curing agent), a formulating component (F)(ii),
and, if desired, a solvent component (L)(iii), in
the presence if desired of a catalyst, using as
crosslinker component (D) in the case of the
polyol mixture a polyisocyanate component (B)(iii)
and in the case of the polyurethane prepolymer a
10 polyisocyanate component (B)(iii) or a low
molecular mass polyol component (A3)(ii) and/or a
low molecular mass polyamine component (E), and
adding the formulating constituents individually
or together before, during or after the blending
15 of the individual components.

24. The process of claim 23, characterized in that the
fluorine-modified macromonomer (A1) is prepared by

20 c₁) reacting a fluoro alcohol component (A4) with the
polyisocyanate component (B)(ii) in the presence
if desired of a solvent component (L)(ii) and in
the presence if desired of a catalyst, the
reaction conditions and the selectivities of
25 components (A4) and (B)(ii) being chosen such that
only one isocyanate group of component (B)(ii)
reacts with component (A4), and subsequently

c₂) if desired, reacting the preadduct from stage c₁)
30 completely with the functionalizing component
(C)(ii), the reaction conditions and the
selectivity of component (C)(ii) being chosen such
that only one reactive group of component (C)(ii)
reacts with the free isocyanate group(s) of the
35 preadduct.